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**(58) Field of search**

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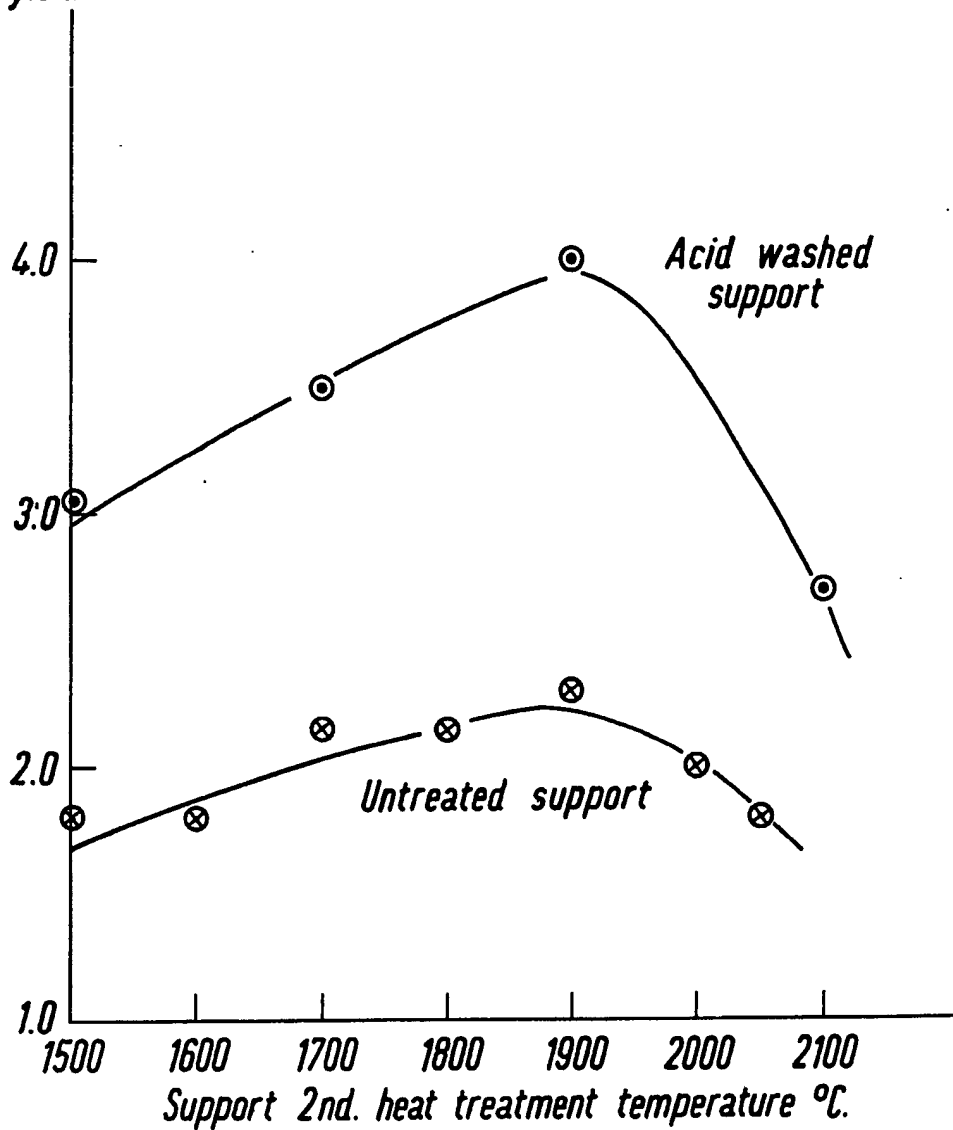
**(54) Catalyst for the production of  
ammonia**

**(57) A catalyst is prepared which  
comprises a transition metal, e.g.,  
ruthenium, and a modifying metal,  
e.g., an alkali metal supported on a  
graphite—containing carbon sup-  
port having specified surface area  
properties which has been washed  
with a concentrated solution of a  
strong mineral acid and then with  
water before impregnation with the  
other components. It is suitable for  
use in the production of ammonia.**

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Maximum ammonia  
yield % Wt.



## SPECIFICATION

## Catalyst for the production of ammonia

- 5 This invention relates to a catalyst suitable for the production of ammonia. 5
- With increased pressure on the world's food resources the demand for nitrogen-containing fertilisers based on ammonia has grown rapidly in recent years. Current Haber processes using nitrogen and hydrogen as feedstock generally use a potassium promoted iron catalyst, usually with other promoters such as alumina. These catalysts are reduced in situ from bulk iron oxides before use and operate under severe conditions, e.g., pressures of up to 300 bars and 10 temperatures of 450°—500°C. 10
- The reaction  $N_2 + 3H_2 \rightleftharpoons 2NH_3$  is highly exothermic and thus the equilibrium is moved to the right at lower temperatures. However, present day commercial catalysts are not sufficiently active at lower temperatures to enable the reaction to reach equilibrium within the short time the 15 reactants are in contact with the catalyst. Activity increases with temperature and therefore a compromise has to be reached. 15
- Recently work by Aika et al, Journal of Catalysis, 27, 424—431 (1972), on the synthesis of ammonia discloses that synthesis over a ruthenium catalyst is promoted by the addition of an alkali metal, particularly when the ruthenium is supported by active carbon or alumina.
- 20 Similarly, British Patent Specification 1367112 to Sagami Chemical Research Centre discloses a complex catalyst for ammonia synthesis which comprises (a) at least one alkali metal belonging to Group 1A of the Periodic Table, (b) at least one compound, preferably a halide, oxide or sulphide, of a transition metal selected from the group consisting of Group 4B, Group 5B, Group 6B, Group 7B and Group 8 of the Periodic Table and graphite. The Periodic Table 25 referred to by Sagami is that given in the "Handbook of Chemistry", edited by Norbert Adolf Lange; McGraw-Hill, 1961; pages 56 to 57. 25
- The complex comprises an alkali metal as the electron donor, graphite as the electron acceptor and a transition metal compound. The alkali metal and the transition metal compound are present as intercalates in the graphite lattice. Aika and Sagami both disclose the use of free 30 alkali metal or precursors thereof, such as azides, as electron donors. 30
- Our copending British Patent Application No. 45711/76 discloses a catalyst comprising (i) as support a graphite-containing carbon having (a) a basal plane surface area of at least 100 m<sup>2</sup>/g, (b) a ratio of BET surface area to basal plane surface area of not more than 8:1, preferably not more than 5:1 and (c) a ratio of basal plane surface area to edge surface area of at least 2:1 and 35 preferably at least 5:1 and (ii) as active component (a) 0.1 to 50% preferably 1—30%, most preferably 5—10% by weight of a transition metal of the 4th, 5th and 6th horizontal Periods of Groups VB, VIB, VIIB and VIII of the Periodic Table expressed as % by weight of total catalyst and (b) 0.1 to 4 times by weight of (a) of a modifying metal ion selected from Groups IA or IIA of the Periodic Table or the lanthanides or actinides, the modifying metal ion being actively 40 associated with the transition metal rather than the support. 40
- Unless otherwise indicated the Periodic Table referred to in the present specification is the Periodic Table published on page B-4 of the Handbook of Chemistry and Physics, 57th Edition, 1976—1977, published by CRC Press, Cleveland, Ohio.
- Such a catalyst is suitable for the production of ammonia from hydrogen and nitrogen and the 45 Fischer-Tropsch reaction. 45
- It is distinguished from the prior art in that it is neither an electron donor-acceptor complex nor is it an intercalate compound.
- The graphite-containing carbon may be prepared by the method disclosed in British Patent Specification 1468441 comprising the steps of (1) an initial heat treatment in an inert 50 atmosphere at a temperature between 900° and 3300°C, (2) an oxidation stage at a temperature between 300° and 1200°C, and (3) a further heat treatment in an inert atmosphere at a temperature between 1000° and 3000°C, preferably between 1400° and 2100°C. 50
- The activated carbons used in the preparation of the support invariably contain significant levels of impurities that can be deposited in the pore mouths during heat treatment resulting in 55 a reduction in the accessible surface area. During or after the preparation the support may also become contaminated with sulphur compounds which subsequently have a deactivating effect. 55
- We have now discovered that washing the support with acid either during the carbon preparation or prior to the addition of the catalytically active substances both removed the sulphur and improves the surface properties of the carbon, thus resulting in a more active 60 catalyst. 60
- Thus according to the present invention there is provided a method for the preparation of a catalyst comprising (i) as support a graphite-containing carbon having (a) a basal plane surface area of at least 100 m<sup>2</sup>/g, (b) a ratio of BET surface area to basal plane surface area of not more than 8:1, preferably not more than 5:1 and (c) a ratio of basal plane surface area to edge 65 surface area of at least 2:1 and preferably, at least 5:1 and (ii) as active component (a) 0.1 to 65

50% preferably 1–30%, most preferably 5–10% by weight of a transition metal of the 4th, 5th and 6th horizontal Periods of Groups VB, VIB, VIIB and VIII of the Periodic Table, expressed as % by weight of total catalyst and (b) 0.1 to 4 times by weight of (a) of a modifying metal ion selected from Groups IA or IIA of the Periodic Table or the lanthanides or actinides, the  
 5 modifying metal ion being actively associated with the transition metal rather than the support, 5  
 which method includes the steps of washing the carbon with a concentrated solution of a strong mineral acid, washing the acid treated carbon with water to remove the acid, then impregnating with a solution of a compound of the transition metal to give the desired concentration and adding a solution of the Groups 1A, 2A, lanthanide or actinide compound to give the desired  
 10 concentration of the modifying metal ion. 10

If the graphite containing carbon is prepared by the method of 1468441, then the acid wash may take place either before the first heat treatment, between the first and second heat treatments or after the final heat treatment.

The preferred transition metals are cobalt, ruthenium and rhodium. Ruthenium is the most  
 15 preferred. 15

Preferred components (b) are the alkali and alkaline earth metal ions. The most preferred are rubidium and potassium.

Suitable strong mineral acids include hydrochloric, nitric and sulphuric acids, preferably the first.

20 Suitable concentrations lie in the range 10% to 80% by volume. 20

According to another aspect of the present invention, there is provided a process for the production of ammonia which process comprises passing a feedstock containing nitrogen and hydrogen over a catalyst prepared as herein before described under conditions of temperature, pressure and space velocity such that conversion to ammonia is effected.

25 Synthesis gas is a suitable feedstock. 25

The Catalyst has a high tolerance of poisons which are normally harmful to conventional catalysts, such as water and carbon monoxide.

Broad and preferred ranges of process conditions are as follows:

		Broad Range	Preferred Range	
	Temperature °C	250–600	300–500	
35	Pressure bars	Atmospheric—300	20–200	35
	Space Velocity v/v/h	1,000—100,000	5,000—30,000	

40 The invention is illustrated by the following example and the accompanying drawing. 40

#### Example

Activated carbon AC 40 supplied by CECA Limited was heat treated to 900°C in nitrogen and the heat treatment continued to 1500°C in argon. It was then oxidised in air at 450°C to 20%  
 45 weight loss. Portions of the oxidised material were then heat treated in argon at various 45  
 temperatures ranging from 1500 to 2100°C to form graphite-containing carbon catalyst supports.

Samples of the latter were then boiled in 40% HCl and subsequently Soxhlet extracted with distilled water until free from chloride ions.

50 Catalysts were prepared by adding 7.5% ruthenium to the supports by impregnation from an 50  
 aqueous solution of ruthenium chloride. After reduction at 500°C in hydrogen for 2 hours 15% rubidium was added from an aqueous solution of rubidium nitrate. After a further heat treatment at 500°C in nitrogen the catalysts were ready for use.

The catalysts were then tested in a 2 ml microreactor at a GHSV of 1000 and a pressure of  
 55 5.14 bar. In each test the temperature was programmed over the range 350°—450°C and the 55  
 maximum ammonia yield noted.

The results obtained are plotted on the accompanying drawing which is a graph in which the temperature of the second heat treatment of the support is plotted against the maximum ammonia yield expressed as a per cent.

60 The graph clearly shows the improved performance of catalysts based on acid treated and 60  
 washed supports.

#### CLAIMS

1. A method for the preparation of a catalyst comprising (i) as support a graphite-containing  
 65 carbon having (a) a basal plane surface area of at least 100 m<sup>2</sup>/g, (b) a ratio of BET surface 65

- area to basal plane surface area of not more than 8:1, and (c) a ratio of basal plane surface area to edge surface area of at least 2:1 and (ii) as active component (a) 0.1 to 50% by weight of a transition metal of the 4th, 5th and 6th horizontal Periods of Groups VB, VIB, VIIB and VIII of the Periodic Table, expressed as % by weight of total catalyst and (b) 0.1 to 4 times by weight
- 5 of (a) of a modifying metal ion selected from Groups IA or IIA of the Periodic Table or the lanthanides or actinides, the modifying metal ion being actively associated with the transition metal rather than the support, which method includes the steps of washing the carbon with a concentrated solution of a strong mineral acid, washing the acid treated carbon with water to remove the acid, then impregnating with a solution of a compound of the transition metal to
- 10 give the desired concentration and adding a solution of the Groups IA, IIA, lanthanide or actinide compounds to give the desired concentration of the modifying metal ion. 5
2. A method according to Claim 1 wherein the graphite-containing carbon has a ratio of BET surface area to basal plane surface area of not more than 5:1 and a ratio of basal plane surface area to edge surface area of at least 5:1.
- 15 3. A method according to either of Claims 1 or 2 wherein the transition metal is present in amount 1 to 30% by weight expressed as % by weight of total catalyst. 15
4. A method according to any of the preceding claims wherein the transition metal is ruthenium.
5. A method according to any of the preceding claims wherein the modifying metal ions are
- 20 rubidium or potassium ions. 20
6. A method according to any of the preceding claims wherein the strong mineral acid is hydrochloric acid.
7. A method according to any of the preceding claims wherein the concentration of the strong mineral acid lies in the range 10 to 80% by volume.
- 25 8. A process for the production of ammonia which process comprises passing a feedstock containing nitrogen and hydrogen over a catalyst prepared as hereinbefore described under conditions of temperature, pressure and space velocity such that conversion to ammonia is effected. 25
9. A process according to Claim 8 wherein the feedstock is passed over the catalyst at a
- 30 temperature in the range 250° to 600°C, a pressure in the range atmospheric to 300 bars and a space velocity in the range 1,000 to 100,000 v/v/hr. 30
10. A process according to Claim 9 wherein the feedstock is passed over the catalyst at a temperature in the range 300° to 500°C, a pressure in the range 20 to 200 bars and a space velocity in the range 5,000 to 30,000 v/v/hr.
- 35 11. A method for the preparation of a catalyst according to Claim 1 as hereinbefore described with reference to the Example. 35
12. A process for the production of ammonia as hereinbefore described with reference to the Example.
13. Catalysts whenever prepared by a method according to any of Claims 1 to 7 or 11.
- 40 14. Ammonia whenever prepared by a process according to any of Claims 8 to 10 or 12. 40